

A comparison of maturity dependent chemical trends in samples from hydrous pyrolysis and naturally matured samples.

Tanja Barth*, Marit Seim and Kristin Skadsem
Department of Chemistry, University of Bergen
Alleg. 41, N-5007 Bergen, Norway

Keywords: Hydrous pyrolysis, asphaltenes, aromatic fraction

Introduction

Hydrous pyrolysis is the method most often used for simulated maturation of source rocks when the aim is to experimentally reproduce the chemical processes of organic matter maturation and petroleum generation as closely as possible. The procedure has been set up so the laboratory conditions correspond to the natural process within the limitations implicit in short-term experiments that do not require sophisticated equipment (1). However, the high temperature/short time procedure (e.g. 250-365°C for 72 hours) compared to the natural situation (80-120°C over millions of years) involve a risk of changes in reaction mechanisms or a decrease in importance of finely balanced energy relationships. The pyrolysis system has a high level of thermal energy which increases the probability of kinetic control of product composition, while thermodynamic control is more probable in the slow processes of the natural low-energy reaction systems.

A major part of petroleum generation consists of the irreversible breaking of carbon-carbon bonds during thermal decomposition of organic matter. Reproducing such processes at increased temperatures and short times should be possible with a reasonable correspondence to the naturally occurring chemical reactions. However, the detailed composition of the products, e.g. isomer composition, homolog distribution etc., should be more liable to be dependent on the reaction rates and temperature levels. Since hydrous pyrolysis is used as a method for chemical reproduction of the natural processes it is important to establish to what compositional levels the simulation is accurate. The molecular maturity markers are good test cases since they often are based on the relative amounts of isomeric forms of the same molecular skeleton. For such compounds there are only small variations in energy levels, and they can be expected to be especially sensitive to artificial effects.

We have compared the patterns of maturity induced change in the chemical composition of two sub-fractions of bitumen in samples from artificially matured source rocks and naturally matured coals. Asphalt fractions are analyzed by FT-IR (Fourier transform infrared) spectroscopy and the maturity related trends are extracted from the spectra by multivariate data analysis. The aromatic fractions of the same samples are analyzed by GC and phenanthrene isomer based maturity parameters are calculated. Multivariate analysis of a larger set of the aromatic components has also been performed.

Experimental

Hydrous pyrolysis: Samples from four immature source rock were artificially matured by hydrous pyrolysis in home-made stainless steel reactors by standard procedures (2). A fixed time of 72 hours and variable temperatures from 250°C to 365°C were used. This gave sets of samples covering the oil generation stage and the start of oil-to gas cracking. A summary of the source rock characteristics is given in Table 1.

The generated bitumen was Soxhlet extracted from the solid residue with dichloromethane (DCM). The extract was combined with the expelled oil collected from the water and reactor surfaces and deasphalted with 40 volumes of hexane. The deasphalted extract was separated into saturate, aromatic and polar fractions by MPLC on a silica column. The aromatic fractions were separated by ring size by HPLC. The maturity of the samples was measured on the residues as vitrinite reflectance, R_o , when possible and by Rock-Eval T_{max} .

Natural samples: A set of 56 coal samples from different sources with R_o ranging from 0.38 to 2.62 (donated by Norsk Hydro, Bergen, Norway) were extracted and fractionated as described for the hydrous pyrolysis samples. The resulting fractions comprise the naturally matured reference set. Asphaltene spectra were recorded from all samples, and the aromatic fractions from 35 samples were also analyzed by GC.

Analytical procedures, asphalt fractions: Diffuse reflectance IR-spectra were recorded using a Perkin Elmer 1720x FTIR-spectrometer interfaced to a Vax computer. 10 μ l of a 5 mg/ml solution of asphaltenes in DCM was deposited as a thin film on a KBr surface, and the solvent evaporated at room temperature. The spectra were analyzed in Kubelka-Munk form. The spectra initially had 3401 data points, but were reduced to 750 variables by a maximum entropy procedure (3). The resulting "condensed" spectra together with maturity measures or hydrous pyrolysis temperature comprise the matrices for multivariate data analysis of maturation trends.

Analytical procedures, aromatics: Aromatic fractions from Series I and II and the coal samples were analyzed. Both the whole aromatic fractions and the isolated three-ring fractions were analyzed by GC on a 50 m CP-Sil-5-CB column with FID-detection. The resulting chromatogram was directly registered in a VG Multichrom laboratory data system. The identification of specific components were based on retention times and comparisons with standards, and confirmed by GC-MS. As concentration measures, both peak heights and areas from the automatic integration were used together with manually measured peak heights. The methylphenanthrene parameters F_1 and F_2 (4) were calculated from the phenanthrene isomer ratios and used as maturity parameters. 30 peaks over the whole range of components were selected for multivariate analysis.

Data analysis: Multivariate analysis to establish patterns of chemical change calibrated to maturity measurements were performed by PLS (Projection to Latent Structures) using the Sirius program for chemometric multivariate analysis (5). Target rotated components were used to visualise the sum of maturity dependent changes in the spectra or chromatograms.

Results

FTIR of asphaltenes: Visual inspection of the IR-spectra to some degree shows the expected maturity trends in all sample sets, with increase in C-H and C=C aromatic stretching and decrease in C=O stretch, but the trends are difficult to quantify directly. However, the maturity components of the spectra extracted with multivariate analysis by PLS describe more than 90 % of the variation in all sample sets, and give well-fitted models. Fig.1 gives an overview of the results for source rock III, a Brent coal, with representative spectra after variable reduction, the target projected maturity component and the fit of the calibration model to the data points. Fig.2 gives an equivalent presentation of the naturally matured samples. Table 2 gives a qualitative summary of the maturity dependent changes for all the data sets. Clear similarities in the maturity dependent trends are observed. Series I shows most deviation. This can be caused by the initially very immature state of the brown coal sample, which gives a different range of maturation than the other series.

However, quantitative comparisons of the different series of hydrous pyrolysis samples and the naturally matured samples is not successful. The multivariate calibration models cannot be used to predict pyrolysis temperatures or maturity parameters for samples from other sets. The model based on the spectra of the naturally matured samples does not correctly predict maturity from the spectra of the artificially matured samples. The similarities in the asphaltene IR spectra thus reflect similar chemical trends with maturity, but the correspondence is not sufficient to be a basis for quantitative measurements or an universal calibration model.

GC of aromatics: The indices gave a reasonably good linearity with measured vitrinite reflectance for the naturally matured coals, as shown in Fig.3a. For the hydrous pyrolysis samples no trend was observed for either of the data sets analyzed. Series I is shown for comparison in Fig 3b. The multivariate analysis for maturity dependent trends is shown in Fig. 3c and d, where the naturally matured samples give inverse isomer loadings, i.e. negative correlations between the amounts of α and β isomers. The hydrous pyrolysis samples only give a negative correlation of the more volatile components with the less volatile components, and no isomer separation in either of the hydrous pyrolysis series.

Conclusion

The standard hydrous pyrolysis procedure which is used for simulating the chemical processes of organic matter maturation can reproduce overall chemical changes in a qualitative manner, as observed in IR-spectra of asphaltenes. The detailed isomer distributions between single components in the aromatic fraction is not reproduced. This indicates that hydrous pyrolysis should be used with caution as a method for simulating natural processes on a molecular level.

References

- 1: Winters, J.C; Williams, J.A.; Lewan, M.D. Adv. in Organic Geochemistry 1981, 1983, 524-533
2. Barth, T.; Borgund, A.E. and Hopland, A.L. Org. Geochem. 1989, 14, 69-76
3. Karstang, T.V. and Eastgate, R.J. Chemolab. 1987, 209-219
4. Kvalheim, O.M.; Christy, A.A.; Telnæs, N.; Bjørseth, A. Geochim.Cosmochim.Acta, 1987, 51, 1183-1888.
5. Kvalheim, O.M. Chemolab. 1988, 4, 11-25.

TABLES:

Table 1: Source rocks for hydrous pyrolysis.

Source rock	Initial maturity	TOC %	S ₂ mg/g	Max.final maturity	No. of exp.
I: Brown coal	0.25 %R _o	53.3	58.1	1.53 %R _o	10
II: Kimmeridge	0.29 %R _o	51.3	333	T _{max} 513	11
III: Brent	T _{max} 428	39.6	32.8	T _{max} 525	8
IV: Heather	T _{max} 424	5.03	22.1	T _{max} 536	7

Table 2: Maturity trends in IR-spectra of asphalt fractions.

Sample	O-H ca cm ⁻¹	C-H aro.	C-H ali.	C=O	C=C	C=O acid	C-H ali.	-O- eth.	C-H aro
	3700- 3100	3100- 3000	3000- 2850	1765- 1690	1630	1575 1520	1450 1380	1400- 1050	880 -700
I	-	+	+	-	+	-	+	-	
II	+	+	-	-	+				+
III		+	-		+				+
IV	+	+	-						+
V ¹		+	-	-	+		+		+

1: Naturally matured samples

Figure 1.
IR-spectra, target component
and fit of model for series I
Brent coal pyrolysis samples.

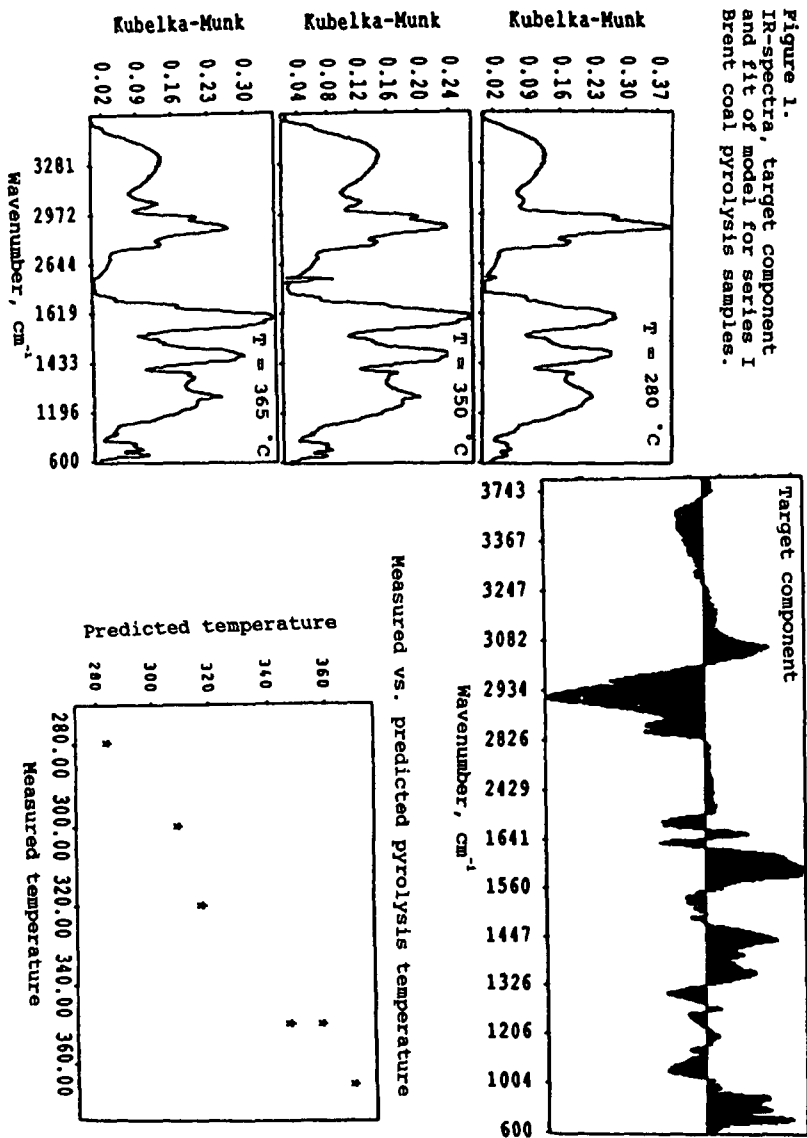


Figure 2.
IR-spectra, target component
and fit of model for series V
naturally matured coals.

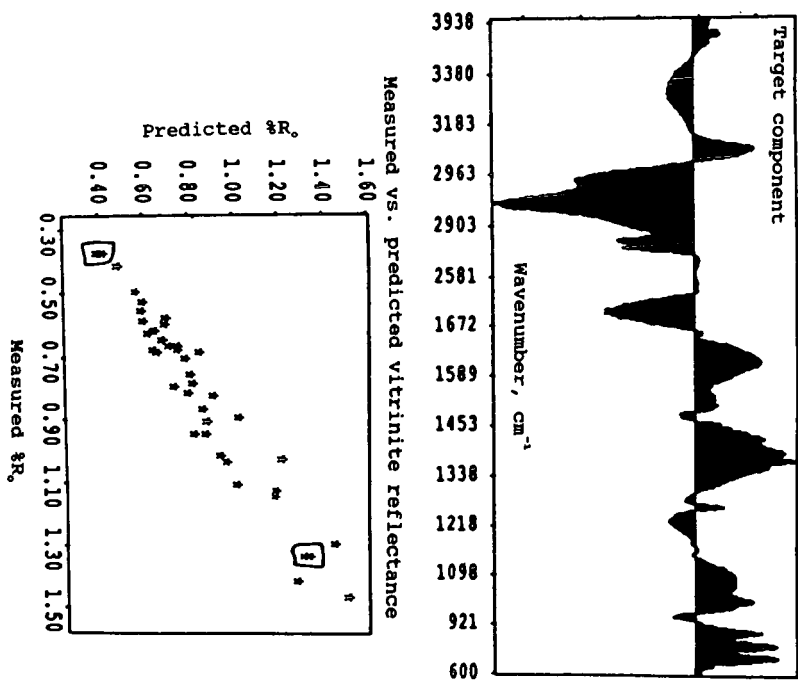
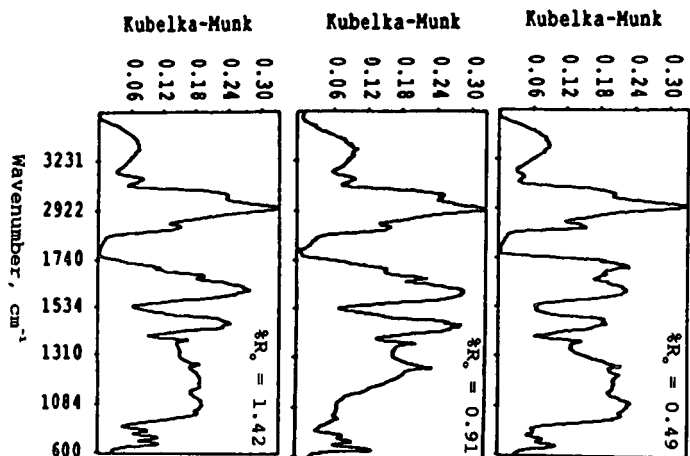


Figure 3.
Methylphenanthrene indices and maturity components
for V - coal samples and I - pyrolyzed brown coal.

